

Platinum-Doped Diamondlike Carbon Thin-Film Electrodes

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INTRODUCTION

Electrodes of diamondlike carbon (DLC) can appear an inexpensive, hence, more practicable alternative to crystalline diamond electrodes which attract great attention, during the last decade, owing to their extraordinary corrosion resistance [1]. Recently we showed [2] that wide-gap diamondlike carbon is not in itself electrochemically active; however, it acquires the electrochemical activity upon introducing admixture of platinum into the DLC bulk during the film deposition.

EXPERIMENTAL

Films of amorphous diamondlike carbon were grown on silicon substrates. The films were prepared using magnetron sputtering of a graphite target in Ar + C₆H₁₂ gas phase. The working gas pressure in the reaction chamber was ca. 10⁻³ Torr; the temperature, 300 to 320 K. The films were approximately 70 nm thick. The platinum content in DLC was determined by an *in situ* X-ray monitoring of the film density. The Pt content varied from 0.5 to 15 at. %.

We took potentiodynamic curves for Fe(CN)₆³⁻ reduction and Fe(CN)₆⁴⁻ oxidation with a linear potential scanning. The differential capacitance was measured in the 1 Hz to 100 kHz frequency range using a Solartron spectra analyzer (model 1250). A 0.5 M H₂SO₄ solution was used as indifferent electrolyte.

RESULTS AND DISCUSSION

For electrodes with relatively high Pt content, the potentiodynamic curves have characteristic current peaks of the reagents' oxidation or reduction. The very shape of the curves with the current peak, whose position in the potential scale depends on the potential scanning rate, shows that the charge transfer at the electrode/solution interface proceeds relatively rapidly, hence, the reaction rate is essentially limited by the reagents [Fe(CN)₆³⁻ or Fe(CN)₆⁴⁻] mass transfer in solution.

We took the cathodic peak current density j_c [at a constant Fe(CN)₆³⁻ concentration and the potential scan rate] as a merit of the electrodes' electrochemical activity. The interrelation between this quantity and the Pt content in the DLC film bulk is shown in Figure (curve 1). On the films containing less than 3 at. % of Pt, no reaction is observed, like on the platinum-free wide-gap DLC electrodes [2]. When the Pt content reaches ca. 9 at. %, the current peak height saturates. In the intermediate region (5 to 7 at. % of Pt), a smaller limiting current, rather than the current peak, can be observed on the potentiodynamic curves, which has a kinetic, rather than diffusion, nature. Thus, an increase in the platinum content in DLC films results in the facilitation of the electrode reaction; it is particularly remarkable that this dependence has a threshold character.

When the Pt content in DLC increases, the

differential capacitance C also increases. We see from Figure (curve 2) that the dependence of C on the Pt content, unlike that of j_c , is gradual, rather than threshold. Obviously, this increase in C results from the Pt metal atoms or clusters appearing at the film surface. Whereas the resistivity of the DLC films does not correlate with the Pt content. Thus, platinum is not a dopant in the diamondlike carbon in the sense adopted in the semiconductor physics: it does not increase the free carrier concentration. Neither is the percolation threshold reached, that is, the Pt particles do not form a continuous structure within the carbon matrix, which would facilitate the current flow through the DLC films. Therefore, we believe that the effect of Pt admixture on the DLC electrode behavior is purely catalytic.

The observed threshold dependence of the electrochemical activity of DLC films on the Pt content can hardly be explained in terms of a uniform medium. We therefore assume that both the DLC bulk conductance (due to sp²-hybridized carbon areas) and the Pt effect on the charge transfer at the electrode/solution interface are nonuniform in their nature. With increasing concentration of platinum in the DLC, the distance between the Pt clusters decreases both in the film bulk and on its surface. When some threshold Pt concentration (ca. 3 at. %) is reached, the distance between the Pt clusters and the nearest sp²-hybridized states on the surface drops down to some critical value which ensures their effective charge carrier exchange. Thus, an effective current flow occurs both in the electrode bulk and through the electrode/solution interface.

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